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Applicants:	Shinya Ishigaki, Nobuhiro Yamada Yoshinori Mashiko, Shoji Yoshimi Shoji Yoshimi, Mikio Yoneoka Osamu Hashimoto, Akira Ishiwada Hisashi Otsuka	)
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Pittsburgh, Pennsylvania

APPENDIX: MARKED UP VERSION OF AMENDED PARAGRAPHS

Paragraphs beginning at line 7 on page 1 and ending on line 29 of page 5:

-- Background Art

Recently, in the major cities, town gas is obtained by evaporating liquefied natural gas (LNG). However, to produce town gas from LNG requires the facilities for maintaining the received LNG at an extremely low temperature under -162°C and for evaporating the LNG to produce town gas. Accordingly, it is not suitable for small or medium-sized businesses to produce town gas from LNG. Further, it is [forecasted] forecast that LNG [becomes] will become scarce [in resources] as a resource in the near future. Accordingly, it is desired that town gas [is] be made from feed stock [except] other than LNG or, from substitute natural gas (SNG). [And so] Accordingly various methods for producing town gas have been proposed.

① Methods using hydrocarbons as feed stock;

There are methods for producing town gas from hydrocarbons, such as liquefied petroleum gas (LPG) and naphtha. Japanese Patent Publication No. 51134/1987 discloses a method for producing gas containing methane (CH_4) as a main component, hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO), by means of steam reforming of hydrocarbons of carbon number 2 to 14 with the catalyst containing nickel, cerium and alumina. And Japanese Patent Opening Gazette No. 144089/1980 discloses a method for producing gas containing methane as a main component, by means of steam reforming of heavier hydrocarbons with the catalyst containing ruthenium. Further, Japanese Patent Opening Gazette No. 17003/1987 discloses a method for producing gas containing methane as a main component, by means of steam reforming of desulfurized hydrocarbons with the catalyst containing ruthenium.

② Methods using alcohols as feed stock;

There are methods for producing town gas from alcohols, such as methanol (CH_3OH) or a mixture of methanol and water (H_2O). Japanese Patent Publication No. 24835/1982 discloses a method for producing fuel gas of higher heating value where a gas containing methane, hydrogen, carbon dioxide and carbon monoxide, is produced by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium, followed by methanation of [those] the produced hydrogen and carbon monoxide. And Japanese Patent Opening Gazette No. 156196/1987 discloses a method for producing methane by a single step by contacting methanol or a mixture of methanol and water with the catalyst containing ruthenium and lanthanum as essential components.

Further, Japanese Patent Opening Gazette No. 234499/1989 discloses a method for [efficiently] efficient evaporation of liquid phase methanol and water, which are heated by the heat of outlet gas of a reactor and are contacted directly with recycled gas. Japanese Patent Opening Gazette No. 304184/1989 discloses a method for separating carbon dioxide from gas

produced by the reaction between alcohol and steam, using liquid phase alcohol. Japanese Patent Opening Gazette No. 123737/1991 discloses a reactor of the type which recovers reaction heat to utilize this evaporation and preheat of feed stock.

And, we have not been able to find out the Prior [Arts] Art regarding a method for producing town gas from dimethyl ether as feed stock.

The above methods ① using hydrocarbons as feed stock require the facilities for desulfurization, supply of hydrogen used for the desulfurization, and hydrogen recycle, since such hydrocarbons as naphtha contain sulfur compounds. Further, sulfur in hydrogen sulfide produced on desulfurization process, is generally fixed as zinc sulfide. It cannot help in treating the zinc sulfide as industrial wastes since zinc sulfide is difficult to decompose and reuse, which causes environmental problems in the future.

The above methods ② use methanol as feed stock in many cases. Since methanol has been desulfurized in the course of production, desulfurization facilities are not newly required in these methods. In this respect, these methods are superior to the above methods using hydrocarbons as feed stock. However, producing town gas from methanol is carried out according to the following reaction equation, theoretically;

$CH_3OH \rightarrow 0.75CH_4 + 0.25CO_2 + 0.5H_2O$

That is, 0.75 mol carbon element in CH_3OH is converted into CH_4, and 0.25 mol of that are converted into CO_2. At this time, 0.5 mol of H_2O (water corresponding to 28% of the weight of methanol) is also produced. In point of transportation of feed stock, it is not economical since potentially reproduced water, not being fuel, is transported. Further, on the production of town gas, it is needed to evaporate the water when evaporating methanol. Accordingly, energy is unnecessarily consumed. Furthermore, it requires liquefied petroleum gas as carburant to make the town gas.

Accordingly, it is an object of this invention to provide a method for producing town gas, in which a sulfur component is not contained in the feed stock, so desulfurization facilities are unnecessary, and cryogenic storage facilities are also unnecessary, and transport efficiency is higher, and extra energy is not consumed on the evaporation process of feed stock, and liquefied petroleum gas is unnecessary as carburant, and which is suitable for small or medium-sized businesses to carry out.

Disclosure of Invention

The above object can be solved by the method for producing town gas, [of claim 1] as a first claim of the present invention; using dimethyl ether (CH_3OCH_3 or C_2H_6O) as feed stock, and evaporating the dimethyl ether, and reforming the dimethyl ether catalytically under the existence of steam, and producing gas mainly containing methane [mainly].

The dimethyl ether used for feed stock can be crude dimethyl ether containing, alcohols which contain methanol as a main component, and/or water. Such a method for producing town gas is carried out according to the following reaction equation, theoretically:

$$C_2H_6O \rightarrow 1.5CH_4 + 0.5CO_2$$

Coexistent steam functions to suppress temperature rise of the reaction system.

It is evident from the above reaction equation that 0.75 mol of carbon element in 1 mol C_2H_6O is converted into CH_4, and 0.25 mol of that are converted into CO_2, which is similar to the case using methanol as feed stock. However, this method using dimethyl ether is efficient and advantageous from the view of transportation, since H_2O is not reproduced. Further, heat energy is not unnecessarily consumed on the evaporation process of the feed stock.

In a method for producing town gas, [of claim 2 according to claim 1] as a second claim of invention, the quantity of the steam for catalytic reforming is within 10/1 to 0.5/1 molar ratio of steam/dimethyl ether. Necessary [quantity] quantities of the steam is ordinarily obtained

by means of introduction into the reaction system from outside. However, in the case wherein the dimethyl ether contains water beyond some quantity, the steam to be introduced from the outside may be unnecessary. The quantity of the coexistent steam to suppress the temperature rise of the reaction system is reduced and the consumption of heat energy is reduced in the method for producing town gas according to [claim 2] the present invention.

In a method for producing town gas, [of claim 3 according to claim 1] as a third claim of invention, the temperature for the catalytic reforming of the dimethyl ether is within 200 °C to 600 °C, and preferably within 250 °C to 550 °C. Such a method prevents deactivation of the catalyst caused by excess temperature rise of the reaction system.

In a method for producing town gas, [of claim 4 according to claim 1] as a fourth claim of invention, dimethyl ether is supplied to serially installed adiabatic fixed bed reactors, under the existence of steam, by one of the following manners;

① Passing cooling means installed between the reactors, dimethyl ether is supplied serially to the reactors;

② A part of divided dimethyl ether is supplied to the reactors serially, and at the same time, the remaining part of the divided dimethyl ether is supplied to the subsequent reactors.

Such a method suppresses excess temperature rise of the reaction system caused by heat of the reforming reaction in the case of using an adiabatic fixed bed reactor.

In a method for producing town gas, [of claim 5 according to claim 1] as a fifth claim of invention, dimethyl ether is reformed with a fluidized bed reactor or a multi-tubular reactor which is in [a] the form of [the] a single stage or [the] plural stages. Such a method for producing town gas prevents excess temperature rise of the reaction system by simplified equipment.

In a method for producing town gas, [of claim 6 according to claim 1] as a sixth claim of invention, by-produced carbon dioxide is removed from the reformed gas of dimethyl ether. Such a method produces gas of higher heating value not containing incombustible gas.

In a method for producing town gas, [of claim 7 according to claim 6] as a seventh claim of invention, carbon dioxide is removed using any of the following manners;

① Absorption by aqueous alkanolamine solution or heated aqueous potassium carbonate solution;

② Adsorption by pressure swinging;

③ Selective separation by membrane.

Such a method [surely] positively removes carbon dioxide from the reformed gas.

In a method for producing town gas, [of claim 8 according to claim 1] as an eighth claim of invention, hydrogen, carbon monoxide and carbon dioxide, which are by-produced on the reforming process of dimethyl ether, are methanized either before or after removing carbon dioxide from the reformed gas. Such a method furthermore increases [furthermore] the heating value of the produced reformed gas.

In a method for producing town gas, [of claim 9 according to claim 1] as a ninth claim of invention, dimethyl ether used for feed stock is added to the produced reformed gas as carburant. Special facilities for storage or supply of carburant is unnecessary in contrast to such other [carburant] carburants as liquefied petroleum gas, and the heating value of product gas can be controlled so as to adjust to the standardization. - -

Paragraphs on page 6 beginning at line 13 and ending in line 25:

- - Conventionally, dimethyl ether is produced by dehydration of methanol which is produced in advance. However, in recent years, the dimethyl ether tends to be directly produced by the reaction between hydrogen and carbon monoxide as in the following equation;

$4H_2+2CO \rightarrow CH_3OCH_3+H_2O$

In this reaction, CH_3OH is sometimes by-produced besides H_2O. In this invention, not only pure dimethyl ether but also crude dimethyl ether containing alcohols of which the main component is methanol, and/or water, can be used for feed stock. Since dimethyl ether does not contain sulfur components, similar to methanol, desulfurization facilities are unnecessary [on] for the production of the town gas. Further, since the boiling point of dimethyl ether is -25.1 °C, which is close to that of methanol, [the] cryogenic storage facilities as needed for LNG, [is] are unnecessary. - -

Paragraphs beginning at line 26 on page 7 and ending at line 8 on page 9:

- - The reforming reaction of the equation (1) is highly exothermic. Hence, when the temperature of the reaction system rises excessively, the reforming reaction of the equation (1) [becomes] will not [to] proceed toward the right side due to chemical equilibrium. Besides, there is a possibility of the side reaction which produces ethylene (C_2H_4) as in the following equation;

$C_2H_6O \rightarrow C_2H_4+H_2O$

Ethylene deposits resinous material on the surface of the catalyst and prevents the reforming reaction. Accordingly, it is desirable to control the reaction temperature within the above temperature range by cooling the reaction system adequately. In this invention, steam coexists

for reforming reaction of dimethyl ether. The principal purpose of coexistence of steam is to suppress the temperature rise of the reaction system.

However, the coexistence of the steam requires extra thermal energy for heating or cooling the steam, in the whole of the production process of the town gas. Accordingly, it is not economical that the quantity of the steam is beyond 10/1 mole ratio (steam/dimethyl ether)[. And] ,and the preferable quantity of the steam is under 10/1, and more preferably under a ratio of 5/1 [ratio]. However, it becomes difficult to suppress the temperature rise of the reaction system when the quantity of the steam is under a ratio of 0.5/1 [ratio]. Accordingly, a most preferable quantity of the steam is [the] within a ratio of 1/1-2/1 [ratio] in consideration of the steam quantity to be used and [easiness] the ease of temperature control of the reaction system.

As a reactor used for the reaction process of reforming dimethyl ether catalytically, there can be used an adiabatic fixed bed reactor which has no internal cooling means. In this case, special considerations are required for keeping the reaction temperature within the preferable range.

For example, dimethyl ether is supplied to a plurally and serially installed adiabatic fixed bed reactor filled with catalyst, under the existence of steam, according to the following [manners] procedures; ① passing cooling means installed between the reactors, dimethyl ether is serially supplied to the reactors, or ② dimethyl ether is divided into two or more parts, and a part of the dimethyl ether is serially supplied to the reactors, and at the same time, the [remains] remainder of [part of] the dimethyl ether is supplied to the subsequent reactors.

Besides, when a fluidized bed reactor or a multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system is sufficiently cooled down. It may be used in a single stage. The fluidized bed reactor has a perforated plate under a fluidized

layer of powdery catalyst. The powdery catalyst is fluidized by introduction of feed gas through the perforated plate and is cooled down by internal cooling means. The multi-tubular reactor has many reaction tubes filled with catalyst. The outside of the reaction tubes is formed as a jacket and is flowed with a medium for cooling the catalyst. In the case that the fluidized bed reactor or the multi-tubular reactor is used for reforming dimethyl ether, the temperature of the reaction system can be easily controlled with the coexistence of steam. - -

Paragraph beginning at line 17 on page 9 and ending at line 24 of page 9:

- - Both reactions are reversible and absorbent can be regenerated.

② Adsorption by pressure swinging;

CO_2 is adsorbed on silica gel, molecular sieve or active carbon under higher pressure and desorbed under [the] atmospheric or lower pressure.

③ Selective separation by membrane;

Only CO_2 can be separated selectively from the mixture of CH_4 anc CO_2 by a membrane having a large permeability of CO_2, such as polyimide, cellulose ester, or polysulfon membranes. - -

Delete the first paragraph on page 12 beginning at line 1 and ending at line 10 and substitute therefore the following amended paragraph:

- - It is apparent from Table 1 that the latent heat of vaporization of dimethyl ether is smaller than that of methanol, and so the heat energy for vaporization of dimethyl ether is smaller than that of methanol. Further, in the theoretical value of the product of methane per unit volume of transported liquid, dimethyl ether is larger than methanol. In this respect, dimethyl ether is superior to methanol as feed stock to be transported. Furthermore, the heat of dimethyl ether on reforming is [larger] greater. Accordingly, [there can be more efficiently used] the heat

of the reforming reaction <u>can be used more efficiently</u> for vaporization and heating of dimethyl ether as feed stock. As above described, it is more beneficial to use dimethyl ether as feed stock of town gas. - -

Paragraphs beginning at line 9 on page 13 and ending at line 13 on page 14:

- -The reason that the reforming reaction of DME is divided into two, by supplying DME into the first and second reforming reactor 15A, 15B together with the steam, is to prevent depositing resinous materials on the surface of the catalyst in the reactors and deactivation of the catalyst due to sintering, besides the fact that the reforming reaction of DME shown by the above equation (1) [becomes] <u>will</u> not [to] proceed toward <u>the</u> right side in chemical equilibrium when the temperature of the reaction system rises excessively with heat of the reforming reaction, which is <u>an</u> exothermic reaction. In this respect, reforming reactors may be installed serially <u>as</u> three or more. Further, in the case that DME contains <u>enough</u> water [enough], a process flow which does not introduce the steam from outside, is applicable, omitting the water storage 14, the pump 14P and the conduits 1c, 1d from Fig. 1.

DME is supplied serially into the first and second reforming reactors 15A, 15B in the above. However, a part of <u>the</u> DME may be supplied serially into the first and second reforming reactors 15A, 15B, and at the same time, another part of <u>the</u> DME may be directly supplied into the second reforming reactor 15B.

Referring to Fig. 1, DME from the DME storage 11 is divided [into] <u>in</u> two at a downstream point of the heat exchanger 12a. A part of the divided DME is heated at a top <u>portion</u> of the heating furnace 13 through a conduit 1h and then is supplied into the second reforming reactor 15B through the conduit 1g together with the outlet gas of the first reforming reactor 15A.

According to such a [manner] procedure, it is possible to [more] better equalize the load distribution between the first and second reforming reactors 15A, 15B. Equalization of reaction temperature can be facilitated. Further, there can be omitted introduction of the steam from outside when DME sufficiently contains water [sufficiently].

The reformed gas led into the methanation reactor 16 contacts the catalyst which fills the methanation reactor 16. Hydrogen, carbon monoxide and carbon dioxide, which are contained in the reformed gas, are converted into methane as in the above equations (2) and (4), so that the heating value of the reformed gas increases. This methanation reaction is carried out under the conditions of a temperature of 250 to 400 °C and a pressure of 0.49 to 7.84 MPa (5 to 80 kgf/cm^2) in use of the catalyst known for methanation reaction, for example, a catalyst containing alumina, nickel and barium oxide, disclosed in Japanese Patent Publication No. 8810/1988. - -

Paragraph on page 17 beginning at line 26 and ending at line 29:

- - Referring to Fig. 2, DME used for the carburant is sucked to a conduit 2p from a carburant storage with a pump 24P and then the DME is evaporated in an evaporator 20. Further, the evaporated DME is led into the conduit 2n through a valve 20V. [Insteads] Instead, it is possible to use LPG as the carburant. - -

On page 21, and ending in line 30:

- - Reactor : The reactor is made of stainless steel, which has an adiabatic structure substantially shutting out the exchange of heat with the outside. Its internal diameter is 21.4 mm and its length is 1.5 m. In order to measure the temperature distribution of the catalyst layer with a thermocouple, a tube made of stainless steel is inserted into the center of the reactor. The tube

has an external diameter of 3 mm and an internal diameter of 2 mm. The reactor as above described will be defined as an "Experimental Reactor A". - -

Page 23, beginning at line 10 and ending at line 30:

- - The second reforming reactor is an adiabatic reactor [similarly] similar to the first reforming reactor. Its inlet pressure is 1.813 MPa (18.5 kg/cm^2), as gauge pressure. A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1g] in Table 2, which is the gas indicated by [1f], adding DME at a rate of 200 kg-mol/h. Catalyst A of 200 cm^3 is packed into Experimental Reactor A. W/F is 0.5 kg-catalyst•h/kg-DME. Previous to the reaction, the pretreatment of Catalyst A is carried out by a flow of hydrogen at a temperature 350 °C for eight hours under the atmospheric pressure.

As the result of the reaction under the condition of an inlet temperature of 285 °C of the reactor, the temperature of the exit of the catalyst layer rises to 545 °C, equal to that in the first reforming reactor. Further, as the result of analysis of the compositions of the outlet gas of the reactor, it proves that all of the DME [react] reacts and the outlet gas has such a flow rate and composition as indicated by [1k] in Table 2.

③ The methanation reactor

A reaction experiment is carried out under the condition that a feed gas has such a flow rate and composition as indicated by [1k] in Table 2 and that gas from the second reforming reactor is cooled to 280 °C and that the inlet pressure of the methanation reactor, which is an adiabatic reactor, is 1.666 MPa (17 kg/cm^2), as gauge pressure. - -

Page 25, beginning at line 10 and ending at line 22:

- - Reactor : A main body of the reactor is made of stainless steel. Its internal diameter is 53.1 mm and its height is 1.5 m. A sintered metal filter is welded to the lower part of the reactor in order to distribute a feed gas uniformly into the catalyst layer. An enlarged part is formed at the upper part of the reactor in order to prevent [from] the powder of the catalyst [to scatter] <u>from scattering</u> out. Its internal diameter is 102.3 mm and its height is 70 cm. An internal cooler which is a coiled tube made of stainless steel, is arranged in the reactor, in order to cool the reactor by circulating hot water at a temperature of 140 °C. [Its] <u>The</u> total length of the tube is 7 m, and its external diameter is 3 mm and its internal diameter is 2 mm. A tube made of stainless steel is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with <u>a</u> thermocouple. The external diameter of the tube is 3 mm and its internal diameter is 2 mm. - -

Page 27, beginning at line 13 and ending at line 14:

- - Flow rate of source for town gas to be obtained under [the] normal [condition] <u>conditions</u> is 350000 m^3 a day. - -

Delete the paragraph beginning at line 30 on page 27, and ending at line 8 on page 28, and substitute therefore the following amended paragraph:

- - Reactor : Reaction tube is made of stainless steel. Its internal diameter is 21.4 mm and its length is 1.5 m. A jacket made of stainless steel is arranged at the outside of the reaction tubes. Its internal diameter is 81.1 mm. The reactor is so substantially isothermal that the reaction heat is eliminated by circulating hot water at a temperature 140 °C into the jacket. A stainless steel tube is inserted into the center of the reactor in order to measure the temperature distribution of the catalyst layer with <u>a</u> thermocouple. The external diameter of the tube is 3 mm

and its internal diameter is 2 mm. The reactor as above described will be defined as Experimental Reactor C. - -

Paragraph on page 30 beginning at line 1 and ending at line 5:

- - As the result of reaction without the pretreatment of the catalyst, the temperature of gas at the exit of the catalyst layer rises up to 350 °C. As the result of analysis of the composition of the outlet gas of the reactor, all of the DME [react] reacts and it proves that the outlet gas has such a flow rate and composition as indicated by [3h] in Table 4. - -

Paragraph beginning at line 19 on page 30 and ending at line 22 on page 30:

- -Catalyst of 150 cm^3 is packed into Experimental Reactor C. Compositions of this catalyst [contains] contain nickel of 10 wt% in the form of NiO and barium of 3 wt% in the form of BaO, which is supported by an alumina carrier extruded with a diameter of 3 mm and a length of 8 mm. - -

Paragraphs beginning at line 7 on page 31 and ending at line 24 on page 32:

- - Effect of Invention

This invention is [practised] practiced as provided in the above description. Hence, this invention has such [effect] effects as described in the following description.

According to the method for producing town gas, [of claim 1] as a first claim of invention, it is efficient from the view of transportation of feed stock since water is not produced on the reforming reaction of dimethyl ether, which is feed stock. Accordingly, extra heat energy corresponding to water is not needed when evaporating feed stock. Further, the facilities for desulfurization, for supply of hydrogen used for the desulfurization process and for recycling the

hydrogen are unnecessary since a sulfur component is not contained in dimethyl ether. Furthermore, small or medium-sized businesses can [be carried] carry out [by] the method of this invention to produce and supply town gas or substitute natural gas alternatively for LNG since cryogenic storage facilities are unnecessary.

In the method for producing town gas, [of claim 2] as a second claim of invention, [there can be suppressed the] there is suppression of excess temperature rise of the reaction system due to the heat of the reforming reactor of dimethyl ether and [the] extra consumption of heat energy needed to heat the feed stock supplied into the reforming reactor, or to cool the gas reformed in the reforming reactor, since quantity of the coexisting steam is controlled within a proper range. Furthermore, [there can be suppressed] the extra consumption of heat energy needed to heat the feed stock, or to cool the reformed gas, can be suppressed in the case [that] wherein the quantity of [the] steam is large.

In the method for producing town gas, [of claim 3] as a third claim of invention, [there can be smoothly proceeded] the reforming reaction of dimethyl ether can smoothly proceed and [there can be prevented] the deactivation of the catalyst can be prevented since the temperature of the reaction system is controlled within a predetermined range.

In the method for producing town gas, [of claim 4] as a fourth claim of invention, [there can be produced] town gas can be produced with a reactor having simplified equipment since adiabatic fixed bed reactors are plurally and serially installed through cooling means between the reactors for the reforming reaction of dimethyl ether and dimethyl ether is supplied into the reactors so as to suppress the temperature rise with heat of the reaction.

In the method for producing town gas, [of claim 5] as a fifth claim of invention, [there can be produced] town gas can be produced with a single reactor since a fluidized bed